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14. ABSTRACT
A major accomplishment of this project has been that we have resolved nearly all the fundamental problems and demonstrated Second Harmonic Generation as an effective and versatile method for characterizing the solid-liquid interfaces of micron to nanometer size particles buried deep in colloids. We have shown for the first time that SHG from the surface of silver nanoparticles can be detected, and through monitoring the second harmonic light scattering we can determine the mechanism and rates of reactions occurring at the nanoparticle surface. During this process we have found a method to increase the fluorescence quantum efficiency of metallic nanoparticles by orders of magnitude. The results from this project will facilitate the usage of nanoparticles in sensor technology in general and in biomedical imaging.

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Final Technical Report:
Structure and Spectroscopy of Buried Interfaces in Organic Thin Films and Colloids
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A major accomplishment of this project has been that we have resolved nearly all the fundamental problems and demonstrated Second Harmonic Generation as an effective and versatile method for characterizing the solid-liquid interfaces of micron to nanometer size particles buried deep in colloids.

The conceptually as well as experimentally challenging fundamental issues include: How to detect SHG from the surface of particles, such as nanoparticles, with dimensions much smaller than the wavelength of the light? And how to determine the adsorption structure of molecules on a spherically symmetric object? Both problems have been resolved, primarily through extending the power of the Mie scattering theory from linear to nonlinear light scattering and applying it to spherical particles, with experimental verification. We have shown for the first time that SHG from the surface of silver nanoparticles can be detected, and through monitoring the second harmonic light scattering we can determine the mechanism and rates of reactions occurring at the nanoparticle surface. During this process we have found a method to increase the fluorescence quantum efficiency of metallic nanoparticles by orders of magnitude.

The results from this project will facilitate the usage of nanoparticles in sensor technology in general and in biomedical imaging.

The initial part of this project was the completion of the development in relation to the interfacial layer between an organic thin film and the substrate on which it is deposited. In particular, the nature of bonding between the layer of molecules that have great potential as organic semiconducting materials have been determined. Through this work, we have gained important fundamental understanding of molecular film deposition, growth, and crystallization.

In addition, we have shown that SHG can be used to characterize the structure of the interfacial layers of room temperature ionic liquids under externally applied electric field.

Below is a summary of the publications and findings from this project.

I. Publications acknowledging AFOSR support during this grant period:

Tetracene Monolayer and Multilayer Thin Films on Ag(111): Substrate- Adsorbate Charge-Transfer Bonding and Inter-Adsorbate Interaction
J. Phys. Chem. C, 112, 4696-4703 (2008), Grazia Gonella, Hai-Lung Dai, and Thomas J. Rockey

Reactions and Adsorption at the Surface of Silver Nanoparticles probed by Second Harmonic Generation
J. Chem. Phys. [communication], 134, 041104-6 (2011), Wei Gan, Grazia Gonella, Min Zhang and Hai-Lung Dai

Activation of Thiols at a Ag Nanoparticle Surface
Angewandte Chemie Int. Ed. {designated as Very Important Paper}, 50, 6622-25 (2011), Wei Gan, Bolei Xu and Hai-Lung Dai

Determination of adsorption geometry on spherical particles from nonlinear Mie theory analysis of surface second harmonic generation
Phys. Rev. B [Rapid Communication], 84, 121402(R)/1-5 (2011), G. Gonella and H.-L. Dai

A self-assembled, metallo-organic supramolecular frequency doubler
Chem. Commun., 48, 1000-02 (2012), L. A. Burke, G. Gonella, F. Heirtzler, H.-L. Dai, S. Jones, J. Zubieta, A. J. Roche

Nonlinear light scattering and spectroscopy of particles and droplets in liquids
Annu. Rev. Phys. Chem. 63 (2012), DOI: 10.1146/annurev-physchem-032511-143748, S. Roke and G. Gonella

   A preliminary patent application on Metallic Nanoparticles with Saturated Coverage of Thiols for Greatly Enhancing Fluorescence Yield is in preparation and will be filed before the end of this year.


   II. Research Summaries:

A. Adsorption, bonding and intermolecular interaction of linear acenes on metal
        A systematic study of adsorption of linear acenes, from benzene to pentacene, on metal surfaces has been conducted using Temperature Programmed Desorption (TPD), electron energy loss spectroscopy (EELS) and Second Harmonic Generation (SHG) under ultra high vacuum conditions. Previously we have studies the adsorption of benzene, aniline and naphthalene on the Ag(111) surface. For benzene the study revealed two different binding geometries and inter-adsorbate repulsive interaction resulted from local dipole moment at the adsorption site induced by the adsorbate-surface charge transfer bonding. The interface dipole of the benzene-silver complex have been determined to be 5.4 ± 1.8 D. For aniline on Ag(111) there is repulsive inter-adsorbate interactions resulting from a local dipole moment of 4.3 D at the adsorbate-substrate complex. The interface dipole of naphthalene on Ag is 5 ± 1 D, resulting from charge transfer of approximately 0.2 e. At the beginning of this funding period, we examined tetracene on Ag(111) and found revealed strong inter-adsorbate repulsion caused by interaction among interface dipoles resulted from charge transfer bonding. The interface dipole was determined as 8.2 ± 2.1 D, which corresponds to a charge transfer of 0.4 e per tetracene molecule to Ag.

        From the study of the series of molecules a generic picture of adsorption is emerging: The linear acene molecule adsorbs likely in a flat configuration allowing charge transfer bonding to the metal. On Ag, in general, each aromatic ring transfers ~0.1 e and contributes ~10 kcal/mole to the binding energy. The local dipole moment induced by the charge transfer bonding causes strong repulsive inter-molecular interactions.

B. Reactions and Adsorption at the Surface of Silver Nanoparticles probed by SHG

Even though nanoparticles have dimensions much smaller than the optical wavelength and shapes commonly with inversion symmetry, we show, for the first time, direct experimental evidence that Second Harmonic Generation (SHG) can be detected from the surface layer of metallic nanoparticles, in this case 40 nm radius Ag particles. The figure on the left shows the light scattered from a Ag nanoparticle colloid following irradiation with 800 nm light from a Ti-Sapphire femtosecond laser output (Oscillator only). The light is detected slightly off the propagation direction of the fundamental beam as we have learned from our particle size studies of SHG from colloidal particles at which angles we should look for the maximum of the SH light scattered from the metallic nanoparticles. The scattered light consists of two parts, both from the Ag particles: The peak at 400 nm is assigned to SHG. The much weaker and broader band at longer wavelengths is from two-photon excitation induced luminescence. The emission spectrum can be empirically described by a nonlinear least-squares fit using a sum of a squared Gaussian function for the 400 nm peak, as the SH intensity is expected to be proportional to the square of the Gaussian profile of the fundamental intensity, and a Gaussian function for the two-photon luminescence.
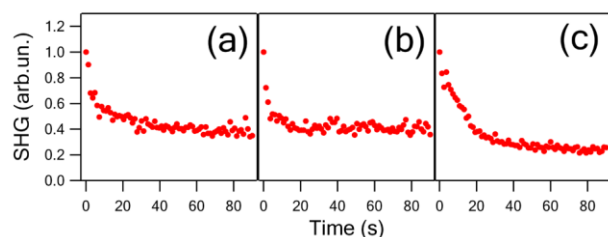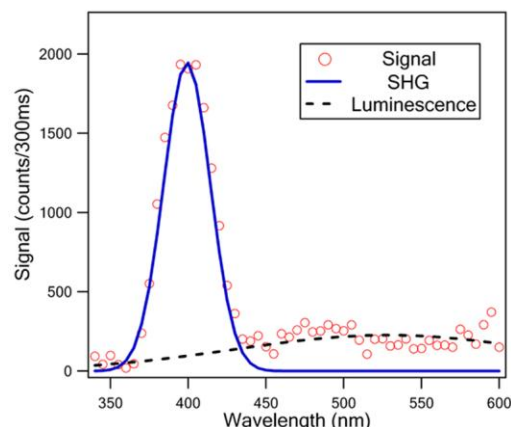
The origin of the SH intensity is unraveled based on its response to the addition of thiol molecules that are known to form strong S-Ag bonds into the colloids. The figure nearby shows substantial decreases upon addition of three types of thiol molecules to the Ag particle surface: (a) 4 µM ethanethiol, (b) 2 µM 1,2-benzenedithiol, and (c) 300 µM sodium 3-mercapto-propanesulfonate. Apparently chemical bonding at the surface localizes the Ag electrons that are responsible for the nonlinear polarizabilty and reduces the nonlinear susceptibility.

The surface generated portion of the SH intensity can thus be used for probing properties and processes at the nanoparticle surface. For example through analyzing the concentration dependent SH intensity decay, we were able to determine the free energy, of adsorption of 1,2-benzenedithiol onto Ag nanoparticle as no larger than -8.8 kcal/mol, i.e. $|\Delta G| \geq 8.8$ kcal/mol.

C. Effect of thiol adsorption on optical properties of colloidal silver nanoparticles

While thiol-metal bonding causes a decrease of the hyper-polarizability of the metal surface, surface bonding may also affect other optical properties of the metallic nanoparticles. It was observed that while SHG from the silver colloid decreases upon the addition of, ethanethiol, the two-photon luminescence (TPL), on the contrary is greatly enhanced. Both phenomena are shown to arise from the same structural change, the formation of strong S-Ag bonds, at the surface which facilitates a variety of electron dynamics that subsequently alter the optical properties of the nanoparticle colloid.

The figure nearby shows that following the addition of a fixed amount of ethanethiol, in this case 10 μM, the TPL signal continues to increase, by nearly two orders of magnitude. Significantly and interestingly, the TPL increase occurs on a time scale (tenths of minutes) a much slower than the SHG decrease (tens of seconds, see above).
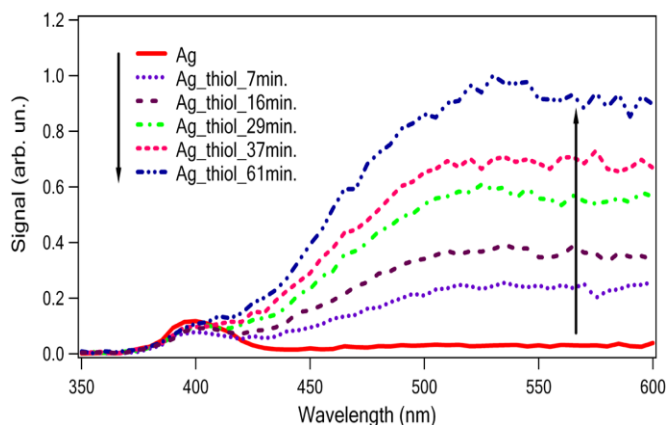
The enhancement of the luminescence signal is an indication that defects or dangling bonds on the silver particle surface were eliminated by thiol adsorption. The surface defects or dangling bonds are known to trap electrons in the excited states and reduce the luminescence efficiency of nanoparticles and quantum dots. The effect of thiol adsorption on the enhancement of the luminescence signal should be quantitatively accounted for by the same adsorption model that is used to describe the SHG decrease. The time lag of the TPL increase with respect to the SHG decrease can be explained by the fact that the effective quenching cross section of a defect is much larger than the physical area the defect occupies. In this case, a substantial amount of the defects has to be eliminated before the effect on TPL becomes appreciable.

D. Reactions of Thiols at Ag Nanoparticle Surface as Activated Processes

The time-resolved SH intensity detected from the surface of the Ag nanoparticles enabled the observations that the thiol adsorption process is temperature dependent. From the adsorption constants determined at three temperatures 303, 293 and 284 K from the SHG measurements, the activation energy barrier for the adsorption of 1,2-benzenedithiol onto the surface of silver nanoparticles in aqueous colloids was determined as (8.4±0.3) *kcal/mol*. (See the Arrhenius plot in the nearby figure.) This energy barrier is too large to be associated with any physical processes such as diffusion and physical adsorption, and is attributed to the formation of the transition state during the bonding reaction.
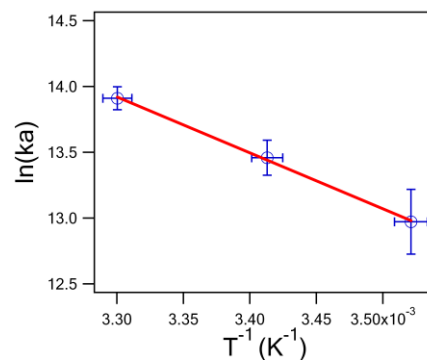
E. Development of Nonlinear Mie Theory for Describing Second Harmonic Generation from the Surface of Spherical Particles

A significant challenge in understanding nonlinear light scattering (NLS) from the surface of a colloidal object is the description of the relation between the scattered nonlinear light and the fundamental light, as well as the influence of the particle strucutre, including its size, shape, materials and surface, on the nonlinear light scattering process. For example, the scattering angular distribution of the SH light generated by molecules adsorbed on a spherical particle depends not only on the directionality of the molecular hyperpolarizability and the adorption geometry, but also the size and refractive index of the particle. How to correctly interpret experimentally observed SHG and relate it to the molecular properties and adsorption

configuration requires rigorous theoretical description of NLS from particles of any sizes and materials.

At present, three main theoretical frameworks are available to describe NLS: the nonlinear Rayleigh-Gans-Debye theory (NLRGD) which we have applied previously, the nonlinear Wentzel-Kramer-Brillouin theory (NLWKB) and the nonlinear Mie theory (NLM). While the first two methods are easier to implement analytically, as they do not require obtaining the exact solution to the Maxwells equations, they are more restrictive in applications due to limitations associated with the assumptions that these models employ: the refractive index mismatch between the particle and the external medium as well as the particle size have to be small. In order to be able to have a theoretical model that can deal with all particle sizes as well as materials, we develop the Mie theory, originally laid out for linear light scattering, for describing nonlinear light scattering from the surface of spherical particles. The figure nearby shows the 3D vies of the SHG intensity scattered from the surface of Au particles with 25 nm radius.
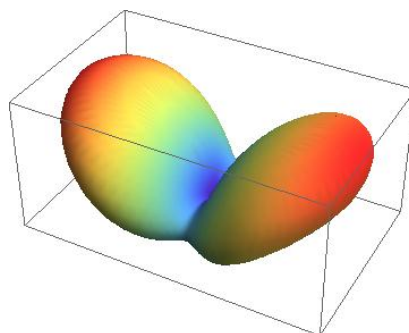
F. Determination of Molecular Hyperpolarizability and Geometry of Molecules Adsorbed on Colloidal Particles

It is highly desirable that we can deduce from the SHG measurements properties such as the hyperpolarizability and the geometry of molecules adsorbed on the particle surface. To correctly interpret the experimentally observed SHG and relate it to the molecular properties and adsorption configuration requires a rigorous theoretical description of SHG from particles of any size and material. Furthermore, how to differentiate the orientation of molecules on a spherically symmetric object, on which ensembles of molecules with different orientations would appear the same in the laboratory frame is a significant conceptual challenge? The nonlinear Mie theory that we have developed can just resolve these issues.

The *first demonstration* of determining the properties of molecules adsorbed on a colloidal particle surface is performed for the model system consisting of malachite green (MG) dye molecules on spherical polystyrene particles in aqueous solutions. The NLM theory analyses enabled the determination that the MG molecule stands nearly upright on the neutral polystyrene particle surface with its C_2 symmetry axis forming an angle within the [$0°$, $38°$] range with respect to the surface normal, and its hyperpolarizability is dominated by the $\beta z''x''x''$ element.
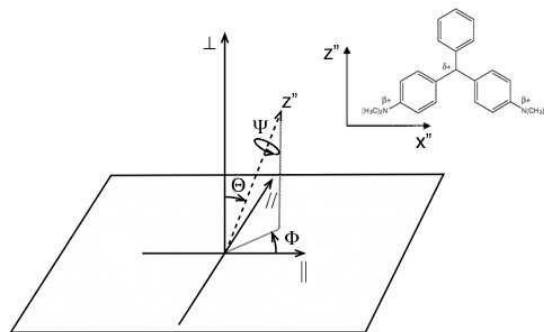
G. A Self-assembled, Metalloorganic Supramolecular Frequency Doubler

In a collaboration with a synthetic laboratory and a theoretical group, we have demonstrated that a dicopper(I) metallocyclophane displays an extraordinarily great SHG effect in solution and thus that self-assembly can lead to highly dipolar metallosupramolecular structures as potent NLO chromophores. It is apparent that, in solution, $[\mathbf{1}_2Cu_2][PF_6]_2$ must consist of the C_2

symmetric form to a significant extent, in spite of the non-NLO active form being preferred in the solid state. Hence, the currently determined value for β_C must be regarded as a *minimum* one for the *pure* C_2-symmetric stereoisomer. The dimeric self-assembly program of ligand **1** with cuprous ion overcomes crystal packing forces, which lead to C_i symmetry in the solid state, to form a majority C_2-symmetric structure in solution. The resulting tetranitro-substituted dicopper(I) metallocyclophane displays an exceptionally strong second harmonic frequency effect ($\beta = (3000 \pm 600) \times 10^{-30}$ esu at 800 nm). Future studies will explore the generality of this paradigm, the design of new ligands whose dicopper(I) metallocyclophanes form polar solids, display improved solubility, allow the evaluation of stereoisomeric equilibria and take advantage of C_2 symmetric structures.

H. Giant Electric Field Induced Molecular Alignment at the Surface of Room Temperature Ionic Liquids

Electric-Field Induced Second Harmonic Generation (EFISHG) from the interfacial Room Temperature Ionic Liquids (RTILs) on a charged conductive ITO (Indium Tin Oxide) film is observed for the first time. The Second Harmonic signal from the RTIL-ITO interface displayed a negative parabolic dependence on the external potential. This observation can be explained and modeled by the interference of the EFISHG from the RTIL interfacial region with the SHG from the ITO film. The analysis shows that the applied potential induces a structural order, likely the alignment of cation orientation, of the RTIL at the interfacial region which facilitated dipole allowed SHG.